

Electronic Supporting Information

ESI Table 1: An overview of current literature reports on the use of metallic-film modified electrodes for the sensing of key metal ion species.

| Electrode Modification | Underlying Electrode | <i>In-/Ex-situ</i> | Target Analyte(s) | Limit of Detection | Technique | Notes / Comments | Reference (within the main text) |
|---|-------------------------------|--------------------|---------------------------|--|-----------|--|----------------------------------|
| <i>Bismuth</i> | | | | | | | |
| Bismuth film | GCE | <i>In-situ</i> | Lead (II) | 1.1 µg/L (5.30 nM) | ASV | One of the first reports into Bismuth Modified Electrodes, explaining that Acetate buffer solution is used to recreate identical conditions to the mercury electrode system. | 50 |
| Bismuth powder mixed within carbon paste | CPE | <i>Ex-situ</i> | Cadmium (II) Lead (II) | 1.2 µg/L (10.67 nM) 0.9 µg/L (4.34 nM) | SW-ASV | Proof of concept demonstrated in a real sample (tap water). Model solution: pH 4.5 0.2 M Acetate Buffer. | 4 |
| Bismuth film | Edge-plane pyrolytic graphite | <i>In-situ</i> | Cadmium (II) Lead (II) | 0.062 µg/L (0.55 nM) 0.084 µg/L (0.40 nM) | SW-ASV | Excellent recovery in spiked river water (100.5 % Cd (II) and 98 % Pb (II)). Model solution: pH 4.5 0.2 M Acetate Buffer. | 11 |
| Bismuth oxide | SPE | <i>Ex-situ</i> | Cadmium (II) | 16 µg/L (142.35 nM) 8 µg/L (38.61 nM) | CCSCP | Proof of concept demonstrated through detection of lead (II) in soil extracts and | 36 |

| | | | | | | | |
|-----------------------------------|---|----------------|--|---|--------|---|----|
| | | | Lead (II) | | | waste water. Model solution: 0.5 M ammonium acetate containing 0.1 M HCl (pH 4.6) | |
| Bismuth film | Graphite-epoxy composite | <i>In-situ</i> | Cadmium (II) Lead (II) Zinc (II) | 2.2 µg/L (19.57 nM) 23.1 µg/L (111.49 nM) 600 µg/L (9230.76 nM) | SW-ASV | Exhibits well-defined, undistorted, reproducible and sharp stripping signals with RSD of 2.99%, 1.56% and 2.19% for Pb (II), Cd (II) and Zn (II) respectively. Application of this electrode towards tap water and soil samples showed promise for the future. Model solution: pH 4.5 0.1 M Acetate Buffer. | 37 |
| Bismuth film | GCE | <i>In-situ</i> | Cadmium (II) Lead (II) Zinc (II) | 0.2 µg/L (1.77nM) 0.2 µg/L (0.96 nM) 0.7 µg/L (10.77 nM) | SW-ASV | Successfully applied to the determination of Pb (II) and Zn (II) in tapwater and human hairwith the results in agreement with atomic absorptions spectroscopy. Model solution: pH 4.5 1.0 M Acetate Buffer. | 38 |
| Bismuth film | Silicon dioxide produced via photolithography | <i>Ex-situ</i> | Cadmium (II) Lead (II) | 1 µg/L (8.89 nM) 0.5 µg/L (2.41 nM) | SW-ASV | Interference caused by Cu (II) was alleviated by the addition of ferrocyanide in the sample solution. Successful determination of Cd (II) and Pb (II) in a phosphate fertilizer and a river water sample. Model solution: pH 4.5 1.0 M Acetate Buffer. | 75 |
| Nafion coated bismuth film | GCE rotating disk | <i>In-situ</i> | Cadmium (II) | 0.1 µg/L (0.88 nM) 0.1 µg/L (0.48 nM) | ASV | Applied towards detection in tap-water, urine and wine. Model solution: pH 4.5 | 39 |

| | | | | | | | |
|--|----------------------|----------------|--|--|--------|--|----|
| | | | Lead (II) Zinc (II) | 0.4 µg/L (6.15 nM) | | 0.1 M Acetate Buffer. | |
| Bismuth oxide | SPE | <i>Ex-situ</i> | Zinc (II) | 33 µg/L (507.69 nM) | SW-ASV | Bismuth oxide present within sensor removing requirement of electrode preparation. Applied towards detection in sea water samples allowing for a limit of detection of 50 µg/L. Model solution: pH 4.5 0.1 M Acetate Buffer. | 44 |
| Multiwalled carbon nanotubes dispersed in Nafion mixed with bismuth | GCE | <i>In-situ</i> | Cadmium (II) Lead (II) | 0.04 µg/L (0.03 nM) 0.03 µg/L (0.14 nM) | DP-ASV | Proof of concept demonstrated in tap water of which the findings were in excellent agreement with atomic absorption spectroscopy. Model solution: pH 4.5 0.1 M Acetate Buffer. | 40 |
| Bismuth film | Carbon film resistor | <i>In-situ</i> | Cadmium (II) Lead (II) Zinc (II) | 0.11 µg/L (1.05 nM) 0.16 µg/L (0.79 nM) 0.008 µg/L (1.30 nM) | SW-ASV | Electrodes were characterised voltammetrically and using electrochemical impedance spectroscopy. Bismuth films deposited galvanostatically and via potential cycling studied for the first time,. Model solution: pH 4.5 0.1 M Acetate Buffer. | 76 |
| Bismuth film | GCE Rotating disc | <i>In-situ</i> | Thallium (I) | 0.21 µg/L (10.8 nM) | ASV | Cadmium interference determined interference from cadmium (II) ions. Model solution: pH 4.5 0.1 M Acetate | 41 |

| | | | | | | Buffer. | |
|--|------------------------------------|----------------|--|---|---------|---|----|
| Bismuth film | Multi-Walled Carbon Nanotubes | <i>In-situ</i> | Cadmium (II) Lead (II) Zinc (II) | 0.7 µg/L (6.22 nM) 1.3 µg/L (6.22 nM) 12 µg/L (184.61 nM) | SW-ASV | Zn (II) could not be determined in the presence of Cu, xylene and PDDA even at low concentration. Model solution: pH 4.5 0.1 M Acetate Buffer. | 77 |
| A mono- or submonolayer of adsorbed bismuth | Mesoporous platinum microelectrode | <i>In-situ</i> | Glucose | 2775.37 µg/L (5 x10 ⁵ nM) ^m | CV | The performance displayed by the non-enzymatic BiMPtEs proposed here suggests wider potential applications with respect to those for classical enzymatic glucose sensors. Examples include glucose detection in media at very low or high pH values, at temperature higher than room values, and for continuous monitoring of glucose in a bioreactor or foods. Model solution : 0.2 M NaOH solution. | 78 |
| Bismuth film | GCE | <i>Ex-situ</i> | Cadmium (II) Zinc (II) | 0.67 µg/L (6.0 nM) 13.00 µg/L (200 nM) | SW-ASV | The stability of the bismuth film under ultrasound was assessed using voltammetric and AFM measurements: after the initial loss, the bismuth film remains intact. Model solution: pH 5.2 0.1 M Acetate Buffer. | 42 |
| Polymer coated-bismuth film | GCE | <i>In-situ</i> | Cadmium (II) Lead (II) Zinc (II) | 2 µg/L (17.79 nM) 2 µg/L (9.65 nM) 6 µg/L (92.30 nM) | SIA-ASV | Polymer coating improves tolerance to surfactants and long-term stability of the electrode whlst increasing potentially time consuming preparatory steps. Model | 43 |

| | | | | | | | |
|---------------------|-----|----------------|--|--|---------|--|----|
| | | | | | | solution: pH 4.5 0.1 M Acetate Buffer. | |
| Bismuth film | GCE | <i>In-situ</i> | Cadmium (II) Lead (II) Zinc (II) Thallium (I) | γ 1.1 μg/L (5.31 nM) γ γ | ASV | Bismuth presence overcomes problem of overlapping peaks for simultaneous measurement of the three analytes. pH 4.5 0.1 M Acetate Buffer. | 79 |
| Bismuth film | CPE | <i>In-situ</i> | Lead (II) | 0.41 μg/L (2.00 nM) | PSA | Simultaneous detection of Pb (II) and Cd (II) using Bismuth film electrode. Model Solution: pH 4.5 0.1 M Acetate Buffer. | 80 |
| Bismuth film | GCE | <i>Ex-situ</i> | Cobalt (II) Nickel (II) | 0.08 μg/L (1.36 nM) 0.26 μg/L (4.43 nM) | ASV | Robust sensor not susceptible to dissolved oxygen when attempting simultaneous sensing of the analytes. Model Solution: pH 9.2 0.01 M Ammonium Buffer. | 81 |
| Bismuth film | GCE | <i>Ex-situ</i> | Cobalt (II) | γ | DP-AdSV | Composition of the plating solution, the influence of accumulation potential, and the stability of bismuth coating as well as the memory effect is studied. Model Solution: pH 9.2 0.01 M Ammonium Buffer. | 82 |
| Bismuth film | GCE | <i>In-situ</i> | Indium | 10 μg/L (87.09 nM) ^m | SW-ASV | Studies in the presence of Cd (II) and Pb (II). Determined that simultaneous determination of indium, cadmium and lead is possible. Model Solution 0.1 M Acetate Buffer with 0.1M KBr. | 83 |
| Bismuth film | GCE | <i>Ex-situ</i> | 2- | 0.4 μg/L (2.88 nM) | CV | Suitable for both batch voltammetric and | 84 |

| | | | | | | | |
|---------------------|-------------------|----------------|---|---|-------------------------------|--|----|
| | | | nitrophenol 4- nitrophenol 2,4- dinitrophenol | 1.4 µg/L (10.06 nM) 3.3 µg/L (23.72 nM) | | flow amperometric detection of the environmentally significant nitrophenols. Model Solution: Brittion-Robinson buffer | |
| Bismuth film | GCE | <i>Ex-situ</i> | Thiamethoxam | 380 µg/L (1302.66 nM) | DPV | Results were justified by the comparative HPLC/DAD measurements. Model Solution: Britton–Robinson buffer. | 85 |
| Bismuth film | GCE | <i>Ex-situ</i> | Azorubine Ponceau 4R | 300 µg/L (594.71 nM) 100 µg/L (165.43 nM) | DPV | Simultaneous detection of the two azo dyes cannot be done, as their potentials are in the same range. Such detection is only possible using mercury electrodes. Model Solution: 0.5 M HNO ₃ . | 86 |
| Bismuth film | GCE | <i>In-situ</i> | Cadmium (II) Lead (II) Cobalt (II) Nickel (II) | 2 µg/L (17.79 nM) 1 µg/L (4.82 nM) 1 µg/L (16.96 nM) 1 µg/L (17.03 nM) | ASV (Cd, Pb) AdSV (Co, Ni) | Simultaneous detection of Pb (II), Cd (II) and Zn (II) using the bismuth film electrode, within a fertiliser sample. Model Solution: 1.0 M Acetate Buffer. | 87 |
| Bismuth film | Iridium microwire | <i>In-situ</i> | Cadmium (II) Lead (II) | 1.5µg/L (13.35 nM) 1 µg/L (4.82 nM) | SW-ASV | Applied to determination in wastewater and tapwater samples. Model Solution: pH 4.5 0.1 M Acetate Buffer | 88 |
| Bismuth film | GCE | <i>Ex-situ</i> | Cadmium (II) Lead (II) | 10 µg/L (88.97 nM) 10 µg/L (48.26 nM) 10 µg/L (153.85 nM) | ASV | Zn (II) detection hindered through the presence of aluminium. Model Solution: PIPES buffer solution. | 89 |

| | | | | | | | |
|---|------|----------------|---------------------------|---|--------|---|----|
| | | | Zinc (II) Indium (III) | 10 µg/L (8.71 nM) | | | |
| Bismuth film | BDDE | <i>In-situ</i> | Cadmium (II) Lead (II) | 2.3 µg/L (20.46 nM) 1.9 µg/L (9.17 nM) | SW-ASV | Pb (II) and Cd (II) could not be detected simultaneously at a bare BDDE, whilst on a bulk Bismuth macro electrode the limits of detection for the simultaneous determination were ~ ten times higher. Model Solution: pH 1 0.1M HClO ₄ . | 10 |
| Gold nanoparticle-graphene-cysteine composite modified bismuth film | GCE | <i>In-situ</i> | Cadmium (II) Lead (II) | 0.1 µg/L (0.88 nM) 0.05 µg/L (0.24 nM) | SW-ASV | The developed electrode displayed a good repeatability and reproducibility. These studies imply that the gold nanoparticle-graphene-cysteine composites might be an alternative candidate for practical applications in electrochemical detection of metal ions. Model solution: pH 4.5 0.1 M Acetate Buffer. | 90 |
| Bismuth film electrode modified with mesoporous silica nanoparticles | GCE | <i>In-situ</i> | Cadmium (II) Lead (II) | 0.6 µg/L (5.39 nM) 0.2 µg/L (0.97 nM) | SW-ASV | The modified electrodes admirable stripping performance for Pb (II) and Cd (II) detection was attributed to the increased surface area and mass transfer on the electrode surface due to the incorporation mesoporous nano-silica. Model Solution: pH 4.5 0.2 M acetate buffer. | 91 |
| Bismuth film electrode | GCE | <i>In-situ</i> | Cadmium (II) | 0.1 µg/L (0.90 nM) 0.05 µg/L (0.24 nM) | SW-ASV | The study concluded that functional nanocomposites based on the thiol-ene | 92 |

| | | | | | | | |
|---|-----|----------------|---------------------------|--|--------|---|----|
| modified with electroreduced graphene oxide-supported thiolated thionine | | | Lead (II) | | | chemistry may offer high application potential to treatment and analysis of environmental heavy metals. Model solution: pH 4.5 0.1 M Acetate Buffer. | |
| Bismuth film | SPE | <i>In-situ</i> | Cadmium (II) Lead (II) | 0.5 µg/L (4.45 nM) 0.8 µg/L (3.86 nM) | SW-ASV | The disposable electrode demonstrated high selectivity for the target metal ions determination and was applied to quantitatively analyze Cd (II) and Pb (II) levels in milk sample extracts with satisfactory results. Model solution: pH 4.5 0.1 M Acetate Buffer. | 93 |
| Bismuth Film | GCE | <i>In-situ</i> | Cadmium (II) Lead (II) | 0.005 µg/L (0.045 nM) 0.04 µg/L (0.19 nM) | ASV | This study utilises a 12 mm GCE and uses double deposition, gaining exceptional limits of detection, due to the large size of the working electrode. Model solution: pH 4.5 0.1 M Acetate Buffer. | 94 |
| <i>Antimony</i> | | | | | | | |
| Antimony film | GCE | <i>In-situ</i> | Cadmium (II) Lead (II) | 0.7 µg/L (6.23 nM) 0.9 µg/L (4.34 nM) | ASV | Convenient operation in acidic solutions of pH 2 or lower (which is superior to that reported for Bismuth films) in the presence of dissolved oxygen. Model solution: pH 2 0.01 M HCl. | 22 |

| | | | | | | | |
|----------------------------------|----------|----------------|--------------------------------------|---|-------------------------------|--|----|
| Antimony film | CPE | <i>In-situ</i> | Cadmium (II) Lead (II) | 0.8 µg/L (7.12 nM) 0.2 µg/L (0.97 nM) | ASV | The practical applicability of the proposed electrode was successfully ascertained via measurement of cadmium and lead ions in the real sample of lake water. Model solution: pH 2 0.01 M HCl. | 24 |
| Antimony film | GCE | <i>Ex-situ</i> | Cadmium (II) Lead (II) Ni (II) | 1.1 µg/L (9.79 nM) 0.3 µg/L (1.45 nM) 6 µg/L (102.23 nM) ^m | ASV (Cd, Pb) AdSV (Ni) | The antimony-film revealed favourable electroanalytical performance similar to that of the in-situ prepared antimony-film and comparable to bismuth- and mercury-based electrodes. Model solution: pH 1 0.1 M HCl. | 95 |
| Antimony film | GCE | <i>In-situ</i> | Cadmium (II) Lead (II) | 1.4 µg/L (12.46 nM) 1.2 µg/L (5.79 nM) | SIA-ASV | The presence of KSCN in the sample solution offers the possibility of detecting ions with more negative oxidation potentials like Zn(II), Mn(II) or Cr(III). Model solution: pH 1 0.1 M HCl. | 96 |
| Macroporous antimony film | Gold | <i>Ex-situ</i> | Cadmium (II) Lead (II) | 0.7 µg/L (6.23 nM) 0.5 µg/L (2.41 nM) | ASV | Further studies would optimise the pore structure and study the limits of this enhancement effect. Model solution: pH 1 0.1 M HCl. | 97 |
| Antimony film | CPE | <i>In-situ</i> | Indium (III) Thallium (I) | 2.4 µg/L (20.91 nM) 1.4 µg/L (6.85 nM) | Stripping Chronopotentiometry | Potential selective determination of Tl (I) in the presence of Ir (III) and Zn (II) is discussed. Model solution: pH 1 0.1 M HCl. | 98 |
| Antimony film | Titanium | <i>Ex-situ</i> | Nickel (II) | 0.2 µg/L (3.39 nM) | SW-AdSV | Novel antimony-sputtered electrodes, | 27 |

| | | | | | | | |
|--|-----------------------------|----------------|---------------------------|--|--------|---|-----|
| | | | | | | fabricated by standard microelectronics thin-film technology. Model Solution: pH 9.2 0.01 M Ammonium Buffer. | |
| Antimony film | CPE | <i>In-situ</i> | Cadmium (II) Lead (II) | 10 µg/L (88.97 nM) 10 µg/L (48.26 nM) | PSA | Simultaneous detection of Pb (II) and Cd (II), using SbF-CPE and BiF-CPE. Model solution: pH 2 0.01 M HCl. | 24 |
| Antimony film | Carbon fiber microelectrode | <i>In-situ</i> | Cadmium (II) Lead (II) | 1.9 µg/L (16.90 nM) 3.1 µg/L (14.96 nM) | ASV | Practical application of the SbFME was demonstrated <i>via</i> measuring Cu (II) in the standard reference solution of natural water. Model solution: pH 2 0.01 M HCl. | 28 |
| Antimony film | GCE | <i>Ex-situ</i> | Sulfasalazine | 310.75 µg/L (780 nM) | SW-ASV | The first application of the antimony film electrode in pharmaceutical analysis. The antimony film electrode revealed favourable electroanalytical characteristics and when compared to its bismuth and bare GCE counterparts. Model solution: pH 2 0.01 M HCl. | 99 |
| Nafion-coated antimony film electrode | Δ | <i>In-situ</i> | Cadmium (II) Lead (II) | 0.3 µg/L (2.67 nM) 0.15 µg/L (0.72 nM) | DP-ASV | The electrode was successfully applied to determining Pb (II) and Cd (II) in vegetable and water samples with satisfactory results. Model solution: pH 2 0.01 M HCl. | 100 |
| <i>Tin</i> | | | | | | | |

| | | | | | | | |
|-----------------|-----|----------------|---------------------------|---|--------|--|----|
| Tin-film | GCE | <i>In-situ</i> | Cadmium (II) Zinc (II) | 0.7 µg/L (6.23 nM) 0.9 µg/L (13.85 nM) | SW-ASV | Extended by exploring the possibility to detect other metals normally determined by ASV Tl (I), Pb (II), Cu (II). Model solution: pH 2 0.01 M HCl. | 29 |
|-----------------|-----|----------------|---------------------------|---|--------|--|----|

^m= Lowest concentration addition recorded

^v = Limit of detection not provided

Δ = Information not accessible

ASV = Anodic Stripping Voltammetry

SW-ASV = Square-Wave Anodic Stripping Voltammetry

DP-ASV = Differential Pulse Anodic Stripping Voltammetry

DPV – Differential Pulse Voltammetry

CCSCP = Constant Current Stripping Chronopotentiometric Measurement

CV = Cyclic Voltammetry

SIA-ASV = Sequential-Injection Analysis Anodic Stripping Voltammetry

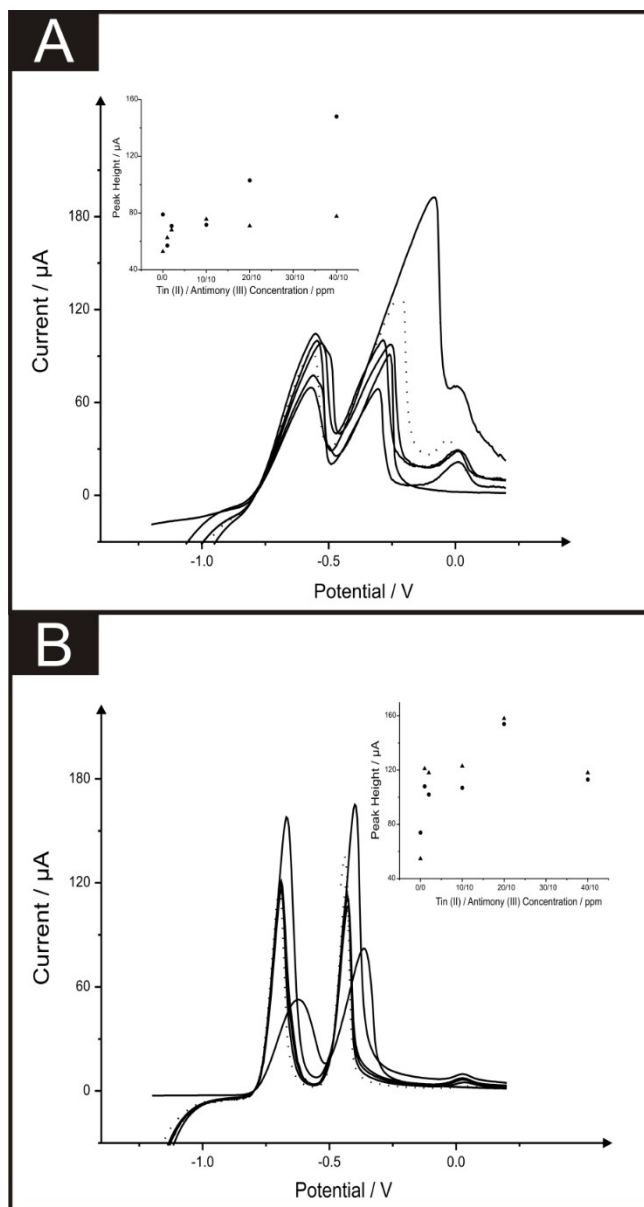
PSA = Potentiometric Stripping Analysis

DP-AdSV = Differential Pulse Adsorptive Stripping Voltammetry

SW-AdSV = Square Wave Adsorptive Stripping Voltammetry

ESI Figure 1

Linear sweep voltammograms resulting from 10 mgL⁻¹ antimony (III) with additions of tin (II) (1 – 40 mgL⁻¹) towards 1030 µgL⁻¹ lead (II) and 560 µgL⁻¹ cadmium (II) in a pH 4.3 acetate buffer solution using both SPE (A) and BDDE (B) (dotted line equates to optimum concentration of antimony (III) and tin (II)). Deposition potential and time: - 1.2 V (vs. SCE) and 120 seconds respectively. Inset: Corresponding plots of voltammetric peak height versus tin (II) / antimony (III) concentration (cadmium (II) – triangles; lead (II) – circles).



ESI Figure 2

Linear sweep voltammograms resulting from additions of 10 mgL⁻¹ and 5 mgL⁻¹ bismuth (III) and tin (II) respectively into a solution containing 1030 µgL⁻¹ lead (II) and 560 µgL⁻¹ cadmium (II) in a pH 4.3 acetate buffer solution using both SPE (A) and BDDE (B) (dotted line equates to optimum concentration of bismuth (III) and tin (II)). Deposition potential and time: -1.2 V (vs. SCE) and 120 seconds respectively. Inset: Corresponding plots of voltammetric peak height versus tin (II) / bismuth (III) concentration (cadmium (II) – triangles; lead (II) – circles).

